

Supporting information

Fabrication and application of ratiometric and colorimetric fluorescent probe for Hg²⁺ based on dual-emissive metal-organic framework hybrids with carbon dots and Eu³⁺

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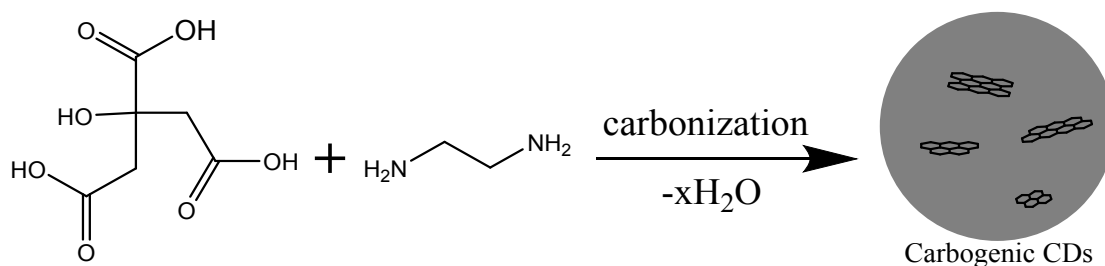


Fig. S1 A synthetic route using citric acid and ethylenediamine to form carbogenic CDs in aqueous solution.

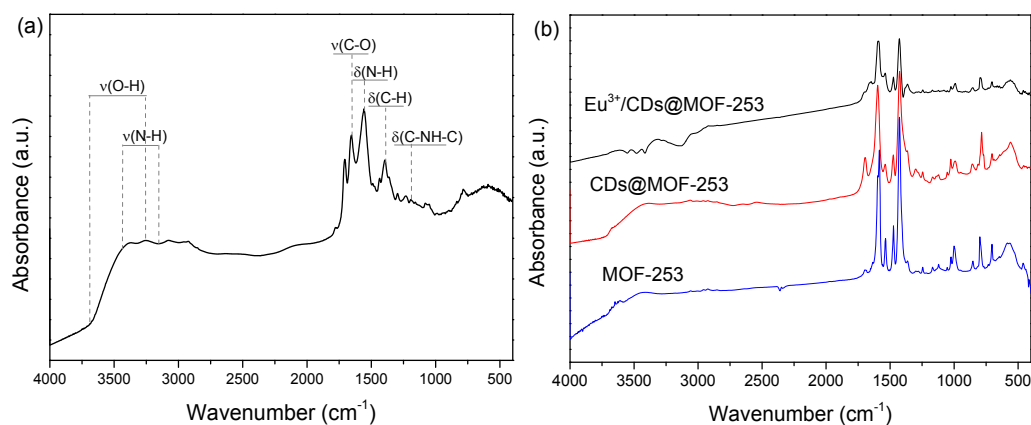


Fig. S2 FTIR spectra of (a) CDs and (b) MOF-253, CDs@MOF-253 and $\text{Eu}^{3+}/\text{CDs@MOF-253}$. In the FTIR analysis of CDs, broad absorption bands at $3000\text{--}3500\text{ cm}^{-1}$ are assigned to $\nu_{(\text{O-H})}$ and $\nu_{(\text{N-H})}$. The hydrophilicity and stability of CDs in aqueous system can be improved by this functional groups. The following were observed simultaneously: $\nu_{(\text{C-NH-C})}$ at 1126 cm^{-1} , $\delta_{(\text{N-H})}$ at 1570 cm^{-1} , and the $\nu_{(\text{C=O})}$ at 1635 cm^{-1} .^{S1}

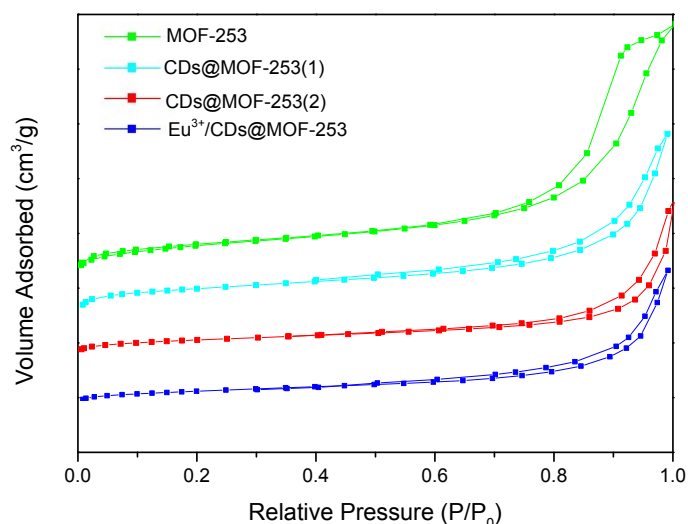


Fig. S3 N_2 adsorption and desorption isotherms of MOF-253, CDs@MOF-253 (the CDs content is 100 mg for (1) and 200 mg for (2)) and $Eu^{3+}/CDs@MOF-253$. The BET surface areas of MOF-253, CDs@MOF-253 (1), CDs@MOF-253 (2) and $Eu^{3+}/CDs@MOF-253$ were calculated to be 723, 386, 215 and 207 m^2/g . And the N_2 sorption isotherms and BET surface area are considerably different from the previous work.^{S2} We speculate the following points which are different from others could be responsible for this: 1) Sodium acetate has been added for size adjustment in our work; 2) Our reaction vessel (15 mL) is a bit smaller than the reported one; 3) The much higher dried temperature under dynamic vacuum on a Schlenk line cannot be achieved in our work.

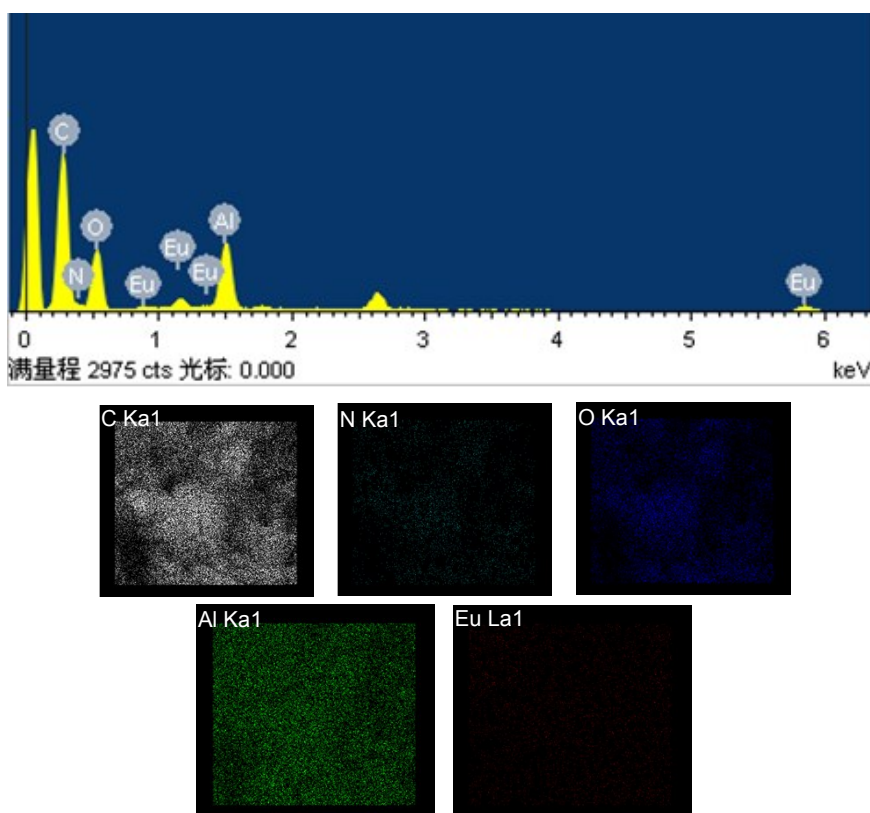


Fig. S4 EDS pattern and SEM mapping of as-prepared $Eu^{3+}/CDs@MOF-253$ samples.

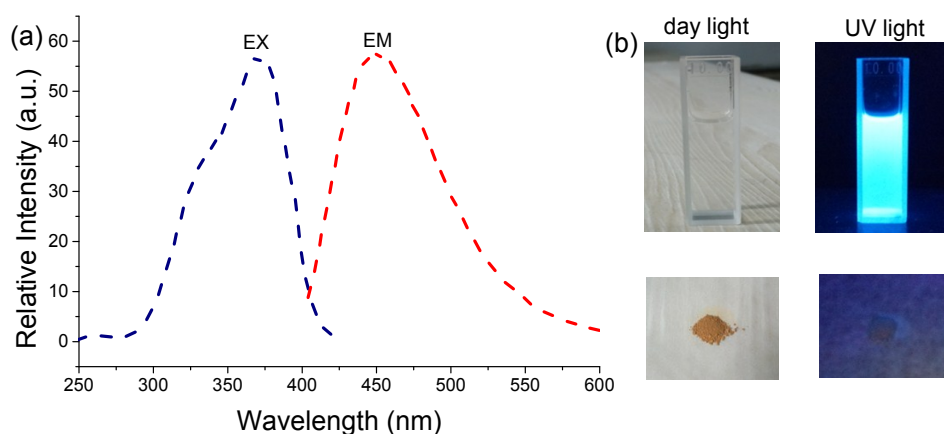


Fig. S5 (a) Room temperature excitation (blue line) and emission spectra (red line) of CDs aqueous solution; (b) the corresponding photographs of CDs solution (top) and dried CDs (bottom) under day light and UV light irradiation at 365 nm.

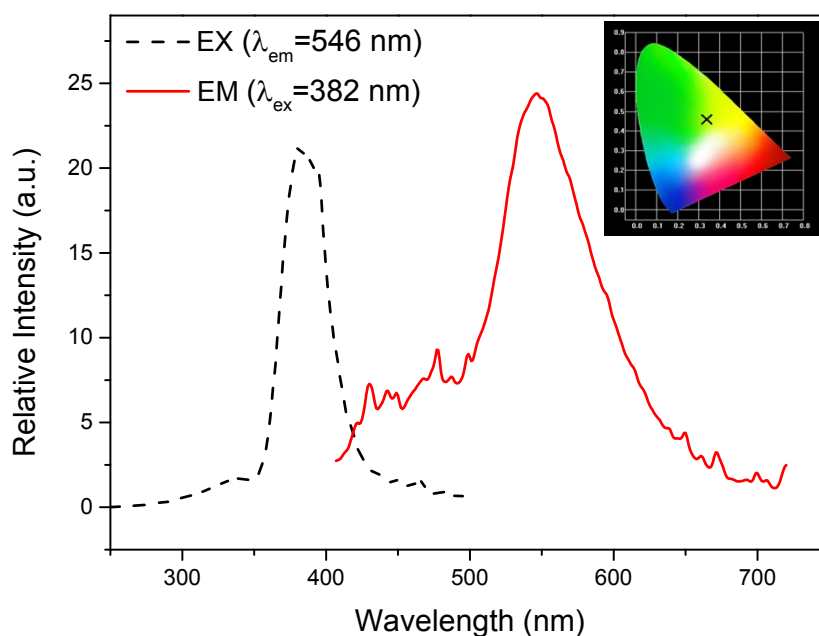


Fig. S6 Room temperature excitation (black line) and emission spectra (red line) of MOF-253 in aqueous environment. The inset is its corresponding CIE chromaticity diagram.

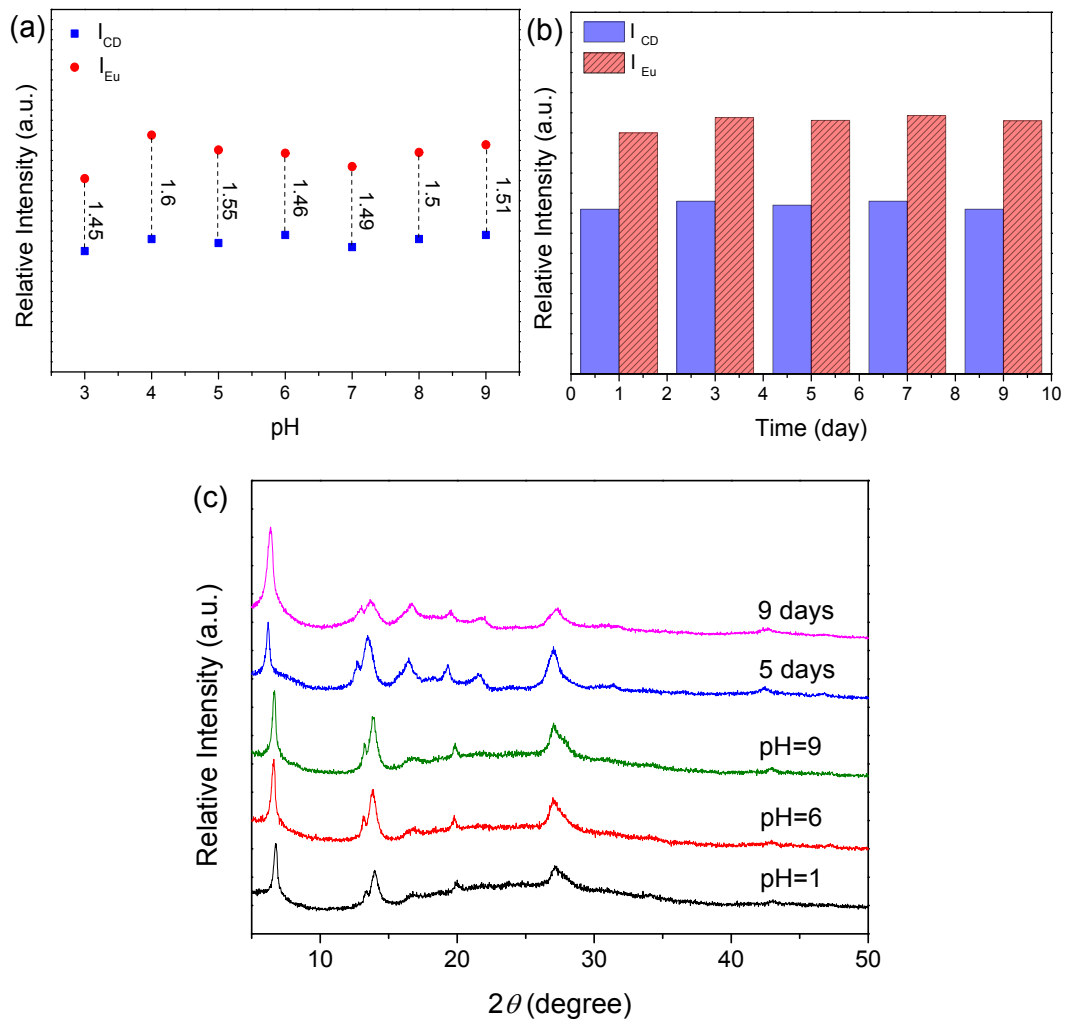


Fig. S7 Stability of PL intensity of $\text{Eu}^{3+}/\text{CDs}@MOF-253$ (a) after immersing in different pH aqueous solutions for 1 h and (b) after treated in aqueous solution for 9 days; (c) PXRD patterns of $\text{Eu}^{3+}/\text{CDs}@MOF-253$ after exposure to different pH and different storage time in H_2O .

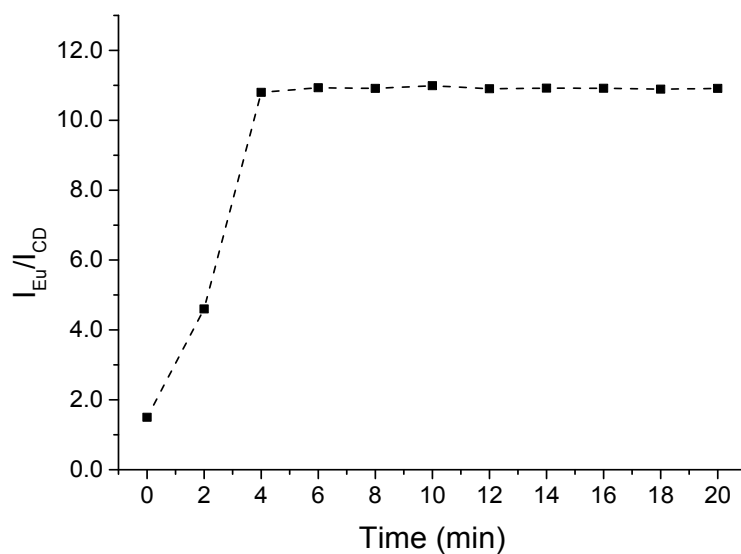


Fig. S8 PL response of $\text{Eu}^{3+}/\text{CDs}@MOF-253$ at I_{Eu}/I_{CD} with immersion time in the aqueous solution of Hg^{2+} (100 μM), $\lambda_{ex} = 360$ nm.

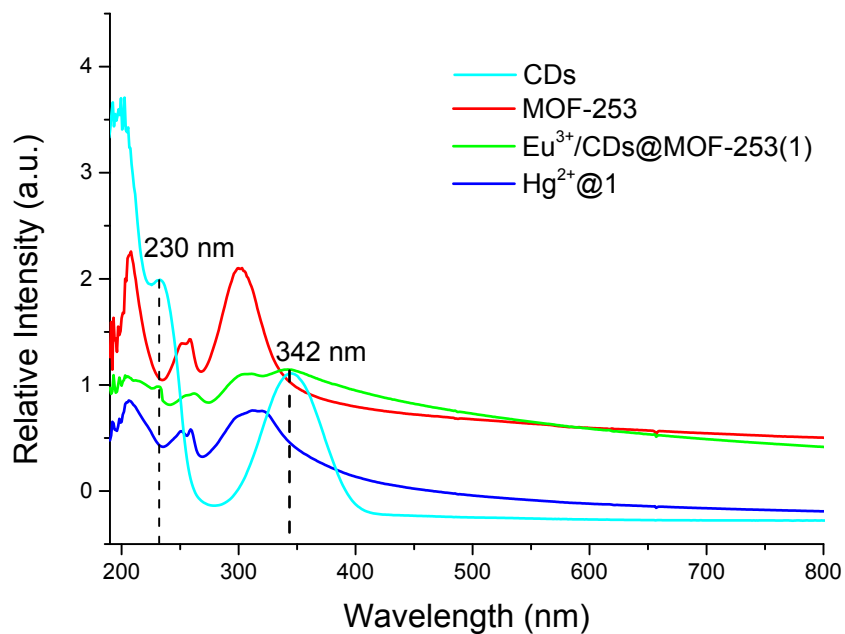


Fig. S9 UV-vis absorption spectra of fine suspensions of powdered CDs, MOF-253, $\text{Eu}^{3+}/\text{CDs}@MOF-253$ and Hg^{2+} treated $\text{Eu}^{3+}/\text{CDs}@MOF-253$ in aqueous solution.

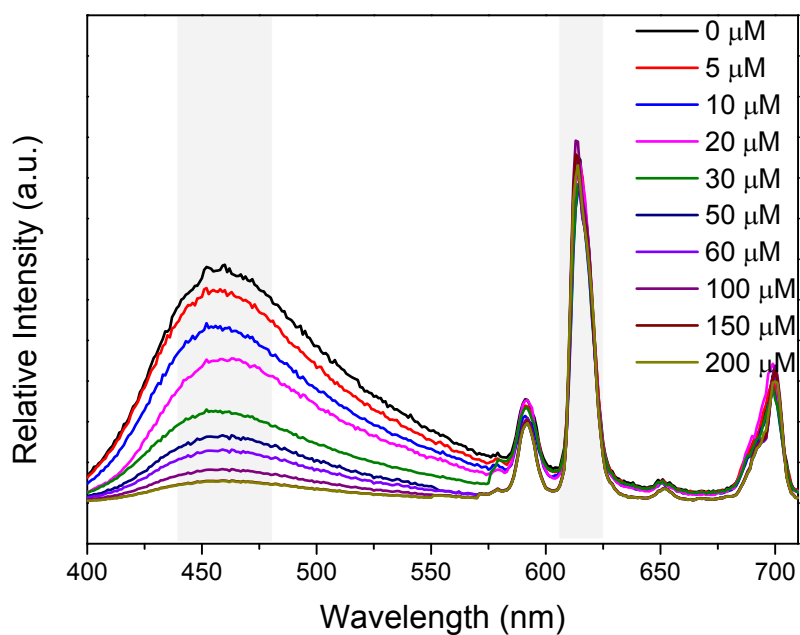


Fig. S10 PL emission spectra of $\text{Eu}^{3+}/\text{CDs}@MOF-253$ in the presence of different concentration (0-200 μM) of Hg^{2+} in aqueous solution, $\lambda_{\text{ex}} = 360 \text{ nm}$.

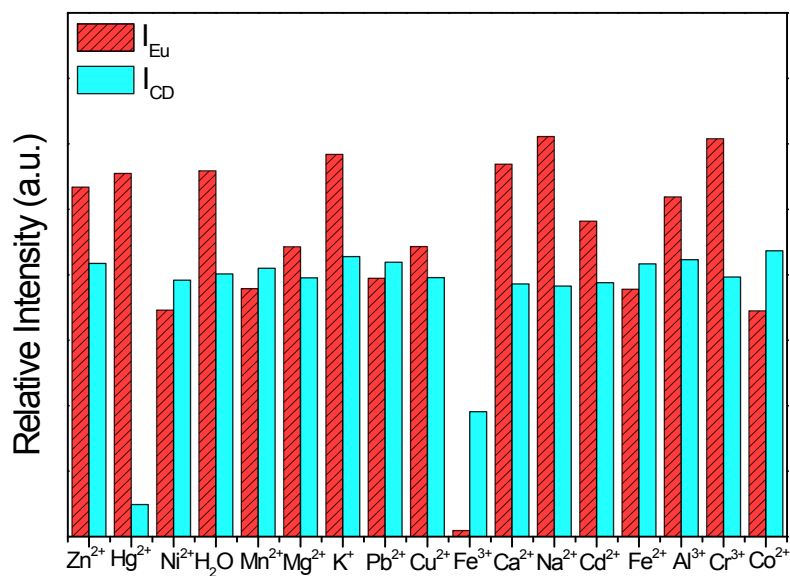


Fig. S11 Selectivity of the $\text{Eu}^{3+}/\text{CDs@MOF-253}$ (3 mg) based sensor for Hg^{2+} over other metal ions (100 μM) in aqueous solution.

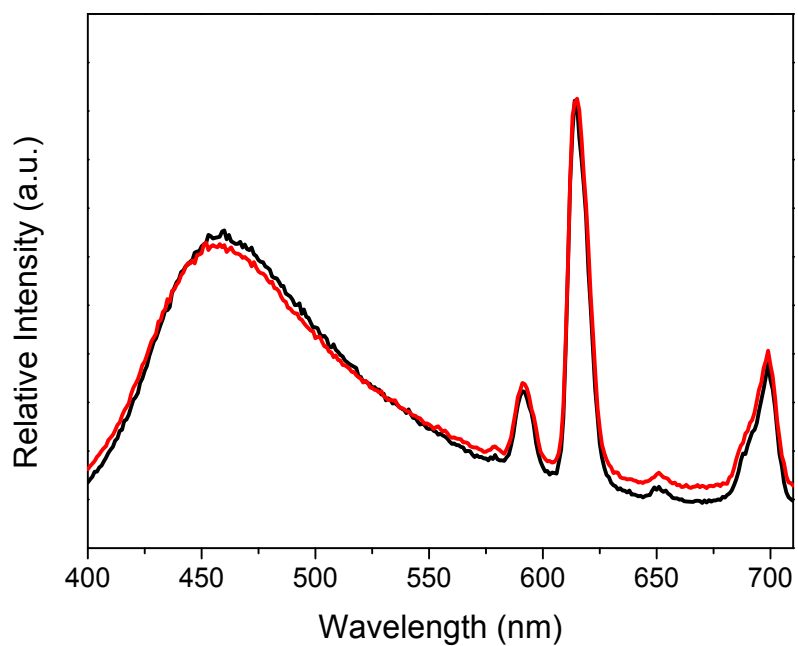


Fig. S12 PL emission spectra of $\text{Eu}^{3+}/\text{CDs@MOF-253}$ in aqueous solution (black line) and in supernatant fluid of Hg^{2+} removal (red line), $\lambda_{\text{ex}} = 360 \text{ nm}$.

Table S1 Hg²⁺ removal ability by Eu³⁺/CDs@MOF-253 in its aqueous solution.

C _{Hg2+} (μM)	M _{Eu/CDs@MOFs} (mg) ^a	I _{Eu} /I _{CD}	C _{Hg2+} (μM)	M _{Eu/CDs@MOFs} (mg) ^a	I _{Eu} /I _{CD}
5	0.3±4.0%	1.48	30	2.0±9.5%	1.43
10	0.6±8.2%	1.45	50	3.5±13.4%	1.44
20	1.0±11.2%	1.52	60	4.0±17.3%	1.41

^a The result was expressed as mean of five measurements ± standard deviation (SD).

References

- S1. a) X. Zhai, P. Zhang, C. Liu, T. Bai, W. Li, L. Dai, W. Liu, *Chem. Commun.*, 2012, **48**, 7955; b) D. Pan, J. Zhang, Z. Li, C. Wu, X. Yan, M. Wu, *Chem. Commun.*, 2010, **46**, 3681.
- S2. a) E. D. Bloch, D. Britt, C. Lee, C. J. Doonan, F. J. Uribe-Romo, H. Furukawa, J. R. Long, O. M. Yaghi, *J. Am. Chem. Soc.* 2010, **132**, 14382; b) F. Carson, S. Agrawal, M. Gustafsson, A. Bartoszewicz, F. Moraga, X. D. Zou, B. Martin-Matute, *Chem-Eur. J.* 2012, **18**, 15337.